Minimum entropy production and the optimization of heat engines

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We consider the problem of minimum entropy production in a heat engine subject only to thermal-resistance losses. For such engines, minimizing the total entropy production is equivalent to minimizing the loss of availability. We show for any engine operating with a given cycle time that minimum total entropy production is achieved in a heat engine by operating it so as to keep the entropy production rate constant along each branch. For the limit of slow engine operation, the entropy production rate should be the same constant for all branches of the cycle. We obtain an expression for the minimum total entropy production and use this to give a bound on the maximum work which can be produced by such engines. This bound is significantly more realistic than the reversible one. Analogous results are derived for a working fluid which carries arbitrary flows from one potential to another.

I. INTRODUCTION

Considerable research effort has been expended recently[1-8] on finding more realistic limits on the optimal operation of heat energies in finite time. This effort was spurred by the economic importance[9] of such limits in connection with decisions concerning the possible benefits which might result from research on various energy consuming or producing processes. Below we present a general framework, which is one step better than the reversible formalism, for finding limits on the operation of heat-engine processes.

Consider a working fluid that absorbs heat from a reservoir at one temperature T_1 and transfers some of the heat to a second reservoir at a lower temperature T_2 while converting the rest of the heat to work (see Fig. 1). Classical thermodynamics analyzes this process under the assumptions:

(1) no friction;

(2) ideal working fluid in internal equilibrium;

(3) heat flows between substances at equal temperatures.

These assumptions give rise to the reversible formalism whose crucial component is the existence of an extra conserved observable called entropy S. The equation expressing the conservation of S completes our otherwise incomplete set of equations and allows us to calculate everything related to the operation of our heat engine. For instance, we can compute the fraction of heat which can be converted to work

$$W/Q_1 = 1 - T_2/T_1 . \tag{1}$$

This result, due to Carnot, provides a limit on the optimal operation of heat engines.

This limit, however, is frequently of little practical importance, because it is achieved only if the heat engine runs reversibly. For real machinery, assumptions (1)–(3) are fulfilled only in the limit that the process is infinitely slow, thus produces zero power. Machinery producing nonzero power must operate in finite time, necessitating losses. Some engines, such as steam turbines driving electric generators, do operate near enough to the reversible limit for the thermodynamic bound to be significant; for others, such as the Otto cycle automobile engine, the reversible thermodynamic

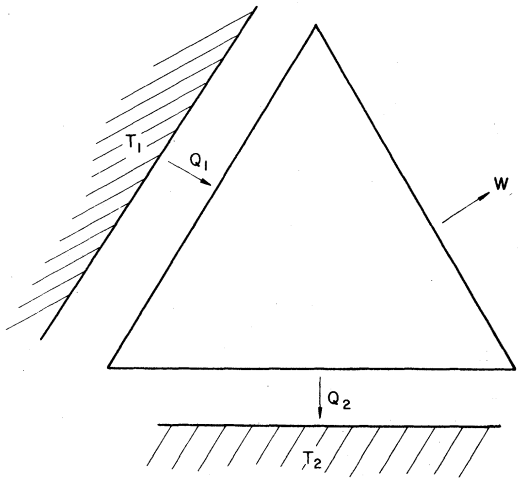

FIG. 1. The flow of heat from reservoir 1 to reservoir 2 while producing work W.

bound has little relevance.

Deviations from ideality in real heat engines may result from many causes, which fall into the following categories[3]:

(i) *heat resistance* of the surfaces which couple the working fluid to the heat reservoirs;

(ii) *friction* of the mechanical linkage which couples the working fluid to the work reservoir;

(iii) *internal losses* in the working fluid such as turbulence, slow chemical reactions, and other unequilibrated degrees of freedom;

(iv) *heat leak* due to imperfect insulation of the two heat reservoirs.

In the present paper, we treat the optimal operation of heat engines under the influence of loss mechanism (i) only. We include this loss mechanism by relaxing assumptions (3) above and replacing it by Newton's law of heat conduction across a boundary. We also assume that

(3′) heat flows between substances in contact through a wall with conductance κ at a rate given by

$$q=\frac{dQ}{dt}=\kappa(T^{ex}-T), \tag{2}$$

where dQ/dt is the heat flux across the boundary separating the temperatures T and T^{ex}. In addition to assumptions (1)–(3′) above, we make the further assumption:

(4) The time involved in the purely mechanical coupling branches is very short and may be disregarded relative to the total cycle time. Mathematically we assume that these processes proceed in zero time. Physically this implies the absence of inertial effects, e.g., when a mechanical branch involves the motion of a piston we assume a piston of zero mass. Assumptions that the mechanical steps involve no losses or zero time have been made also in some previous works on the subject,[6,7] but cannot be used when frictional (type-ii) losses are significant.[3]

The resulting theoretical framework retains the advantage of allowing explicit calculation of all quantities related to the operation of the heat engine, and adds time to the list of variables of the system, thereby making it a thermodynamic system, rather than a thermostatic system. This gives more realistic bounds on work production or consumption. Obviously these bounds depend on the prescribed cycle time.

In previous papers concerning model engines with these loss mechanisms, we have determined the rates at which they operate to optimize efficiency, effectiveness, or power. In this paper we focus on entropy production, taking it as an objective function to determine criteria for optimal operation of heat engines. The main results are stated in Sec. V. These are derived in Secs. VI–VIII for heat engines and generalized in Sec. IX to general flows.

II. HEAT ENGINES

Heat engines may be conveniently classified by the type of cycle undergone by the working fluid. For all the conventionally treated examples, such cycles are made up of branches of the following types: *adiabatic*: $q=0$, the working fluid does not exchange heat with its surroundings; *isothermal:* T^{ex} is a constant, the working fluid is allowed to exchange heat with a constant temperature environment; *isometric:* V is a constant, the working fluid is maintained at constant volume; *isobaric:* pressure P is a constant, the working fluid is maintained at constant pressure; *polytropic*: the working fluid satisfies the relation $PV^n=\text{const}$.

Note that when a heat resistance is inserted between the reservoirs and the working fluid, the external and internal temperatures are no longer the same along isothermal branches; we have chosen to define "isothermal" to mean the external temperature (the reservoir temperature) is kept constant. Below we derive two theorems concerning any heat engine in which the working fluid goes through a cycle made up of branches of the above five types. More generally these theorems apply to any cycle during which we can control the ratio of outside to inside temperatures (T^{ex}/T) on each nonadiabatic branch of the cycle.

Table I shows the kinds of branches that make up the commonly used heat cycles employing gaseous working fluids. Diagrams of these cycles on common scales in the PV and TS planes are shown in Fig. 2. The Carnot cycle is used almost exclusively as a theoretical model, because its excessively high compression and expansion make it impractical. The other cycles serve as conceptual prototypes for the design of real engines. The Stirling and Ericsson cycles are the basis of hot air external combustion engines, which have received considerable attention of late.[10,11] The Brayton cycle has been used mainly for refrigeration, while the Otto, Diesel, and dual combustion cycles are used for internal combustion engines. (Sometimes these cycles are altered so as to use one or more polytropic branches.)

III. THE WORKING FLUID

The Carnot treatment of the operation of a heat engine makes liberal use of the analogy between the extraction of work from the spontaneous flow of water from one height to another and of entropy from one temperature to another. The maximum work extractable is[12,13]

TABLE I. Branches employed in several heat engine cycles.

Cycle	Adiabats	Isotherms	Isometrics	Isobars	Polytropes
Carnot	2	2			
Stirling		2	2		
Ericsson		2		2	
Brayton	2			2	
Otto	2		2		(1-2) [a]
Diesel	2		1	1	(1-2) [a]
Dual combustion	2		2	1	(1-2) [a]

[a] Sometimes polytropes may be used instead of isometrics and isobars.

$$W_{\max}=\sigma(T_1-T_2), \tag{3}$$

where σ is the amount of entropy carried from T_1 to T_2. Graphically, σ is the total width of the TS diagram for any cycle, as shown, e.g., in Fig. 2. For example, if the working fluid is an ideal gas undergoing a Carnot cycle, then

$$\begin{aligned}\sigma &= S(V_1,T_1)-S(V_2,T_2)\\ &= R\ln(V_2/V_1)+C_V\ln(T_2/T_1),\end{aligned} \tag{4}$$

where V_1 and V_2 are the smallest and largest volumes of the gas, and T_1 and T_2 are the highest and lowest temperatures. We make further use of this analogy and view our working fluid as a carrier of entropy. However, our situation is more complicated than Carnot's, because entropy is not only carried, but also created. Nevertheless, the engine in which entropy creation is due only to Newtonian heat-flow constraints turns out to be a fully solvable model of very general applicability. The results follow very simply if we choose the entropy content of the working fluid as the basic parameter and express all other quantities in terms of it.

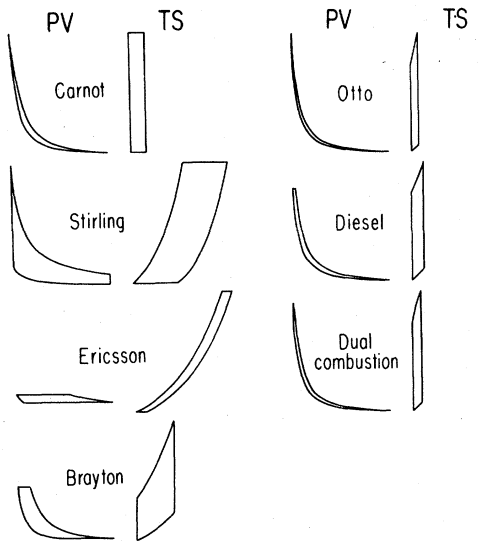

FIG. 2. PV and TS diagrams on common scales for several heat-engine cycles using ideal-gas working fluid. The volume ratio $V^{\min}:V^{\max}$ is 1:10 for all the cycles, and the temperature ratio $T_1:T_3$ is 6:1 for all cycles except the Carnot cycle which has 3:1. (It cannot operate at 6:1 with a volume ratio of 1:10.)

IV. CONTROL PARAMETERS

It might seem that the most natural choices of control variables for operating a heat engine would be the load on the piston and the external or reservoir temperature T^{ex}. These may be used, provided that we know the equation of state of the working fluid. However there is another choice of control variable that is just as practical as the piston load and that makes the analysis much easier, namely the internal temperature T of the working fluid. This quantity can be controlled at any point in a process by introducing a fast (effectively instantaneous) adiabatic compression or expansion to produce the desired change. We may equally well consider such adiabatic steps as controls on the difference between internal and external temperatures, i.e., on the thermal force between the working fluid and the reservoir. We choose to express the optimal control problem in terms of functions $F(T^{ex},T)$; we are free to do so, just as long as these functions are single-valued where we use them. We shall pick the F for each branch of a process to suit the constraints of that branch. For example on "isothermal" branches—strictly, branches with constant T^{ex}—F is controlled by adjusting T; on branches with fixed mechanical coupling,[14] the function F is controlled by adjusting T^{ex}. We shall show how the optimal variation of a properly chosen function $F(T^{ex},T)$ can be obtained so as to give the extremal entropy, without any explicit use of an equation of state.

To end this section we note that throughout our discussion we implicitly assume that the control process requires no time. For the control of internal temperature by mechanical coupling this is already implied by our assumption (4), Sec. I.

V. MAIN RESULTS

Although one can use many different objective functions to define what one means by the "optimal operation" of a heat engine (efficiency, power, entropy production, cost, etc.), we will be concerned with optimal only in the sense of minimizing the total entropy production. This is equivalent to minimizing the loss of availability (see Appendix A), but not to maximizing efficiency or power which were used as objective functions in other works.[1,3-7]

We derive the main theorem below.

Theorem 1. Minimum total entropy production implies constant rate of entropy production on each branch of the process[15]:

$$\min(\Delta S) \rightarrow dS_i/dt = \text{constant for branch } i\,. \qquad (5)$$

These constants depend on the heat conductances along the different branches.

Corollary 1. In the slow-process limit (to be defined in Sec. VII A) dependence of the constants in Eq. (5) on heat conductances disappears, and the optimal operation then implies the same constant rate of entropy production along all branches.

The theorem and its corollary are equally valid for a working fluid carrying any number of fluxes operating in a cycle between any number of reservoirs. The derivations leading to Theorem 1 have a useful byproduct.

Theorem 2. The entropy produced by a heat engine in which the working fluid interacts with heat reservoirs through conductances $\kappa_1, \ldots, \kappa_N$ for a total cycle time $\tau \gg |\sum_i \sigma_i/\kappa_i|$ is bounded by

$$\Delta S \geq \left(\sum_i |\sigma_i|\right)^2/\kappa\tau\,, \qquad (6)$$

where ΔS is the entropy produced,

$$\kappa = \max[\kappa_1, \ldots, \kappa_N]\,,$$

and σ_i denotes the entropy change of the working fluid (i.e., entropy flow into the working fluid) along branch i. This theorem has the immediate corollary[13]:

Corollary 2. The work produced by a heat engine in finite time and subject to heat conduction losses is bounded by

$$W \leq W_{\text{rev}} - T_0\left(\sum_i |\sigma_i|\right)^2/\kappa\tau\,, \qquad (7)$$

where T_0 is the temperature of the environment which defines the proportionality between loss of availability and entropy production (see Appendix A), and where $W_{\text{rev}} = W_{\text{rev}}(T_0)$ is the work available from a reversible process connecting the same initial and final states of the heat sources and sinks.[16]

This section has been worded for heat engines with emphasis on heat conduction. Generalizations to other flows are derived in Sec. IX.

VI. OUTLINE OF METHOD

We use the calculus of variations with the entropy production as the objective function and the fixed cycle time τ as the main constraint for the minimization. The procedure is composed of the following steps:

(1) Divide the total cycle time τ into $\tau_1 + \cdots + \tau_N = \tau$, where τ_i is the time spent on the ith branch with the working fluid in contact with the reservoir at temperature T_i^{ex} through conductance κ_i. [By assumption (4), Sec. IV, branches on which only mechanical energy is exchanged are assumed to proceed in zero time.]

(2) Optimize the time behavior of the working fluid so as to minimize the entropy production on each branch i subject to fixed τ_i and fixed initial and final states of the working fluid.

(3) Given a set of times $\{\tau_i\}$, the results from step (2), and the characteristic limitations of the engine (e.g., compression ratio, temperature, and pressure ranges, etc.) solve for the (unique) consistent set of initial and final states on each branch.

(4) Optimize the allocation of the total time τ among the different branches, that is, determine the values of τ_i, $(\sum_i \tau_i = \tau)$ which minimize the total entropy production per cycle.

The optimization uses two types of variations required by steps (2) and (4). A simple argument shows that this procedure indeed gives the correct optimal cycle. If only one branch of the optimal cycle is varied, the resulting cycle can perform no better. The Euler equations from the one branch optimizations in step (2) express this fact in mathematical terms. These equations are necessary conditions on the optimal cycle but are not by themselves sufficient to determine the optimal cycle uniquely. However, when we carry out step (3) (Sec. VIII) we shall see that these necessary conditions do define a unique optimal path for each specific time allocation τ_i. It remains to determine the optimal times [step (4)]. We do this by finding a second set of necessary conditions which follow from altering the optimal cycle to one with different τ_i but which still satisfies the Euler equations from step (2). The fact that the optimal cycle is extremal with respect to variations in τ_i as well gives us this second set of conditions and completely determines the optimal cycle.

This argument can be expressed as a sequence of inequalities, thus,

$$\Delta S = \sum_i \Delta S_i(\tau_i) \geq \sum_i \Delta S_i^{\text{opt}}(\tau_i) \geq \sum_i \Delta S_i^{\text{opt}}(\tau_i^{\text{opt}}) = \Delta S^{\text{opt}}. \qquad (8)$$

In words, the entropy production associated with the cycle is the sum of contributions (all positive) along each branch. Each of these contributions is at least as large as the entropy produced for the optimal behavior along that branch in the same time τ_i. Further, optimizing the allocation of the fixed total time τ among the τ_i can only decrease (or leave unchanged) the sum.

We now focus our attention on step (2): Optimization along a branch. Here we minimize the value of an integral over a path subject to certain constraints. Though the technique is standard,[17] we reproduce the general formulas here for easy reference.

We start with the control variables $X = (X_1, X_2, \ldots, X_k)$, the time interval $(0, \tau)$ the objective function

$$\Phi = \int_0^\tau \mathcal{L}(X, \dot{X}, \ddot{X}, \ldots)\, dt, \tag{9}$$

and the constraints

$$\begin{aligned} &\int_0^\tau F_i(X, \dot{X}, \ddot{X}, \ldots) dt = \text{const}, \\ &G_j(X, \dot{X}, \ddot{X}, \ldots) = 0. \end{aligned} \tag{10}$$

The path yielding the extremum of Φ subject to the constraints (10), is given by the solution of the Euler-Lagrange equations

$$\frac{\partial L}{\partial X_l} - \frac{d}{dt}\frac{\partial L}{\partial \dot{X}_l} + \frac{d^2}{dt^2}\frac{\partial L}{\partial \ddot{X}_l} - \cdots = 0, \quad l = 1, \ldots, k, \tag{11}$$

where L is the modified Lagrangian,

$$L = \mathcal{L} - \sum_i \lambda_i F_i - \sum_j \lambda_j(t) G_j, \tag{12}$$

$\{\lambda_i\}$ are constant undetermined multipliers, and the $\{\lambda_j(t)\}$ are undetermined multiplier functions of time. This framework will give the same results, of course, in any system of coordinates. When we use the entropy content of the working fluid as a state parameter, the Euler-Lagrange equations reduce to simple algebraic equations, because the Lagrangian does not depend on time or on any time derivative.

The optimization in step (4) is done by standard N-variable calculus techniques, solving the set of algebraic equations

$$d\Phi^{\text{opt}}/d\tau_i - \lambda = 0, \tag{13}$$

where the Lagrange multiplier λ comes from the constraint $\sum_i \tau_i = \tau$. The details of these optimization procedures are provided in the following sections.

VII. DERIVATION FOR THERMAL PROCESSES

A. One branch, internal temperature as control variable

On branch i, the system at temperature $T_i(t)$ is in contact with a heat reservoir at constant temperature T_i^{ex} through a conductance κ_i so that the heat flux is

$$\frac{dQ_i}{dt} = \kappa_i [T_i^{\text{ex}} - T_i(t)]. \tag{2'}$$

Then for the given duration τ_i on the ith branch, the heat flow into the system is

$$Q_i = \int_0^{\tau_i} dQ_i = \int_0^{\tau_i} \kappa_i [T_i^{\text{ex}} - T_i(t)]\, dt, \tag{14}$$

where $T_i(t)$ is as yet undertermined. The entropy change of the system (the flow of entropy into the system) is

$$\sigma_i = \int_0^{\tau_i} \frac{dQ_i}{T_i(t)} = \int_0^{\tau_i} \kappa_i \frac{T_i^{\text{ex}} - T_i(t)}{T_i(t)}\, dt, \tag{15}$$

and the total entropy change is

$$\begin{aligned} \Delta S_i &= \int_0^{\tau_i} \left(\frac{dQ_i}{T_i(t)} - \frac{dQ_i}{T_i^{\text{ex}}}\right) \\ &= \int_0^{\tau_i} \kappa_i [T_i^{\text{ex}} - T_i(t)] \left(\frac{1}{T_i(t)} - \frac{1}{T_i^{\text{ex}}}\right) dt. \end{aligned} \tag{16}$$

Recall that our approach divides the optimization into steps. In step (2), carried out here, the "corners" of the process are fixed with regard to thermodynamic states and time, and we solve for the optimal paths which connect these corners. In step (4), (Sec. VIII), we find the optimal permissible locations of these corners. Fixed corners (i.e., given initial and final states of the working fluid) for each branch i, constrain the values of σ_i, Eq. (15). We are free to include in our optimal path infinitely fast reversible adiabatic segments. These do not enter into the Euler equation. Rather, they serve to connect the optimized segments determined by the Euler equations with the initial and final states, as shown in Fig. 3. Thus the values of the σ_i's are the only constraints that enter into the Euler equations. We take ΔS_i as our objective function and, with T_i^{ex} constant, $T_i(t)$ becomes our control variable. The Lagrangian for the optimization is

$$\begin{aligned} L = {} & \kappa_i [T_i^{\text{ex}} - T_i(t)] \left(\frac{1}{T_i(t)} - \frac{1}{T_i^{\text{ex}}}\right) \\ & - \lambda \left(\frac{\kappa_i [T_i^{\text{ex}} - T_i(t)]}{T_i(t)}\right), \end{aligned} \tag{17}$$

where λ is a constant Lagrange multiplier. The Euler equation is

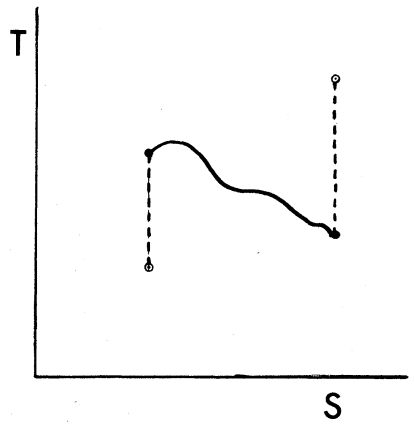

FIG. 3. Arbitrary curve (solid line) spliced to given initial and final states by adiabats (dashed lines).

$$\frac{\partial L}{\partial T_i} = -\kappa_i\left(\frac{1}{T_i(t)} - \frac{1}{T_i^{ex}}\right) - \kappa_i\left(\frac{T_i^{ex} - T_i(t)}{T_i(t)^2}\right) + \lambda\kappa_i \frac{T_i^{ex}}{T_i(t)^2} = 0, \tag{18}$$

because L depends only on T_i and not on any of its time derivatives. Thus $T_i(t)$ is obtained from an algebraic, not a differential, equation, which implies that the solution has no arbitrary constants, and neither the initial nor final values of the control function $T_i(t)$ can be specified arbitrarily. As illustrated in Fig. 3, we are free to include infinitely fast reversible adiabats, and hence we need not be concerned that the solution to the Euler equation will, in general, not fall at $T_i(0)$ and $T_i(\tau_i)$ when $t=0$ and τ_i. Without this freedom, the calculus of variations problem between given initial and final states does not have a solution. This is due to the openness of the set of trajectories over which one optimizes. However, there is a least upper bound to our objective function on this set of trajectories. We can come arbitrarily close to achieving this upper bound by compressing (or expanding) as fast as we can to get to the appropriate Euler solution and, after staying on it as long as possible, expanding (compressing) as fast as possible to get the required final state. Examples of such systems have been worked out recently. This kind of solution is well known in many subjects where optimization methods are used; in economics, they are known as "turnpike" solutions, for example.[9f,18]

We note that, since the only time dependence in Eq. (18) is in $T_i(t)$, this function must be constant, and the optimal trajectory is of the form shown in Fig. 4. Thus heat should be transferred with system and reservoir remaining isothermal at their own temperatures. The internal temperature is

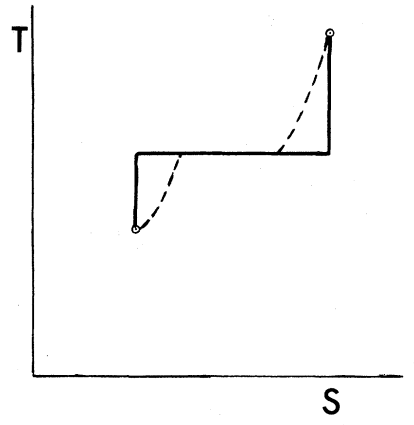

FIG. 4. The form of the optimal branch required by the Euler equation (18). The vertical solid lines correspond to the case in which the adiabats may occur infinitely fast. If there is a constraint limiting the velocity, the system will follow the dashed curves to and from the isotherm (turnpike theorem Refs. 23 and 24); the exact forms of the dashed curves depend on the form of the constraint.

most easily determined from the constraint

$$\sigma_i = \int_0^{\tau_i} \kappa_i [(T_i^{ex} - T_i)/T_i]\, dt = \kappa_i \tau_i (T_i^{ex}/T_i - 1), \tag{19}$$

$$T_i = T_i^{ex}/(1+\sigma_i/\kappa_i\tau_i),$$

so that

$$\Delta S_i = \frac{\sigma_i^2/\kappa_i\tau_i}{1+\sigma_i/\kappa_i\tau_i}, \tag{20}$$

and

$$\frac{dS_i}{dt} = \frac{\Delta S_i}{\tau_i} = \frac{\sigma_i^2/\kappa_i\tau_i^2}{1+\sigma_i/\kappa_i\tau_i} = \text{const}. \tag{21}$$

The value of T_i is thus that value compatible with the entropy change σ_i, the fixed time τ_i, and the requirement that $T_i(t) = \text{const}$.

In the limit in which other processes are slow with respect to heat transfer, i.e., when $\tau_i \gg |\sigma_i|/\kappa_i$, these expressions reduce to

$$\Delta S_i = \sigma_i^2/\kappa_i\tau_i \tag{20'}$$

and

$$dS_i/dt = \sigma_i^2/\kappa_i\tau_i^2. \tag{21'}$$

We call such processes for which $\tau_i \gg |\sigma_i|/\kappa_i$ *slow processes*. For heat engines producing power on the order of 100 kW, realistic values for heat conductance and entropy flows are[19] $\kappa \sim 200$ J/K sec and $\sigma \sim 10$ J/K implying $\sigma_i/\kappa_i \sim 0.05$ sec. (See Appendix B.)

We note in passing that the same conclusion, constant dS_i/dt, is obtained starting from any other

pair of functions chosen from Eqs. (14)–(16) as constraint and objective functions. In particular we may use the heat exchanged and the total entropy produced along the branch as constraint and objective functions, respectively. Here we seek to minimize the total entropy produced for a specified amount of heat exchanged. The role of these functions may also be interchanged: For a prescribed amount of entropy produced, we may determine the extremal heat exchange. In all these cases we obtain in general a Lagrangian which does not depend on time or on any time derivative. The Euler equation for the optimal evolution of the control variable is therefore an algebraic equation involving constants only, thus yielding a constant solution.

B. One branch, external temperature as control variable

We now consider branches on which the working fluid is subjected to some (prespecified) nonthermal coupling. In particular, this category includes isometric, isobaric, and polytropic branches. We can still optimize the thermal interaction by controlling the temperature $T_i^{ex}(t)$ of the reservoir.

As in the previous section we want to minimize the entropy production, ΔS_i for a given transfer of entropy σ_i. In the spirit of Sec. IV, we define a new control variable $x_i(t) \equiv T_i^{ex}(t)/T_i(t)$. The Lagrangian for the system becomes

$$L = \kappa_i(T_i^{ex} - T_i)\left(\frac{1}{T_i} - \frac{1}{T_i^{ex}}\right) - \lambda\kappa_i(T_i^{ex} - T_i)/T_i$$

$$= \kappa_i(x_i - 1)(1 - x_i^{-1}) - \lambda\kappa_i(x_i - 1), \tag{22}$$

and the solution of the Euler equation

$$\partial L/\partial x_i = \kappa_i(1 - x_i^{-2}) - \lambda\kappa_i = 0 \tag{23}$$

is a constant $x_i = 1 + \sigma_i/\kappa_i\tau_i$, so that again the rate of entropy production is constant:

$$\frac{dS_i}{dt} = \kappa_i(x_i - 2 + x_i^{-1}) = \frac{\sigma_i^2/\kappa_i\tau_i^2}{1 + \sigma_i/\kappa_i\tau_i} \tag{24}$$

and the reservoir temperature should be varied so that

$$T_i^{ex}(t) = T_i(t)(1 + \sigma_i/\kappa_i\tau_i). \tag{25}$$

Note that again our solution has no arbitrary constants, and an optimal path exists only between $T_i^{ex}(0)$ and $T_i^{ex}(\tau_i)$ which satisfy Eq. (25). This is why we introduced the assumption of noninertial controls, thereby freeing us from any initial or final conditions on the control functions. For T_i^{ex} this is true by fiat, although for $T_i(t)$ in Sec. VII A it was true because of the freedom to include adiabatic jumps. We have lost this freedom for the present optimizations since we assume that the mechanical coupling is specified, e.g., constant volume.

Note that these expressions for T_i^{ex}/T_i and dS_i/dt are identical to Eqs. (19) and (21) of Sec. VII A, which are obtained with the internal temperature as the control parameter. This is not surprising. We can always perform the optimization in terms of $x_i(t)$; the result $x_i = \text{const}$ is obtained independently of the nature of the branch. The results (19) and (21) are obtained by putting $T_i^{ex} = \text{const}$.

C. Consecutive branches

We are now in a position to allocate the total time among N branches of a process which has been optimized along each branch by the techniques of Secs. VII A and VII B. In doing so we assume that the engine constraints are such that the σ_i's are predetermined independently of the τ_i's for each branch i, making step (3) of our procedure (Sec. VI) unnecessary. Optimization over time allocation is therefore performed taking the σ_i's to be constants. For more general constraints, the σ_i's may be functions of the τ_i's. This point is taken up more fully in Sec. VIII where we show that in the long cycle time limit the σ_i's may always be regarded as constants for the present optimization. For short times the optimization depends on the equations of state of the working fluid and becomes analytically intractable even for the example of an ideal gas in a cylinder. Numerical solutions for this example are given in Appendix B.

If along each branch i the working fluid absorbs σ_i units of entropy in time τ_i through heat conductance κ_i, we want to minimize the total entropy production

$$\Delta S = \sum_i \Delta S_i = \sum_i \frac{\sigma_i^2/\kappa_i\tau_i}{1 + \sigma_i/\kappa_i\tau_i}, \tag{26}$$

for constant total time

$$\tau = \sum_i \tau_i, \tag{27}$$

by varying the individual τ_i (σ_i and κ_i are fixed). We make the substitution

$$\tau_i' = \tau_i + \sigma_i/\kappa_i, \tag{28}$$

so that

$$\Delta S = \sum_i \sigma_i^2/\kappa_i\tau_i', \tag{29}$$

and

$$\tau' = \sum_i \tau_i' = \tau + \sum_i \sigma_i/\kappa_i. \tag{30}$$

Optimizing gives

$$\frac{\partial \Delta S}{\partial \tau_i'} = \frac{\sigma_i^2}{\kappa_i \tau_i'^2} = \lambda \frac{\partial \tau'}{\partial \tau_i'} = \lambda , \tag{31}$$

where λ is a Lagrange multiplier. Solving for τ_i' and evaluating λ by the constraint (27) gives

$$\tau_i' = C|\sigma_i|/\sqrt{\kappa_i} , \tag{32}$$

or

$$\tau_i = C|\sigma_i|/\sqrt{\kappa_i} - \sigma_i/\kappa_i , \tag{33}$$

with

$$C = \tau' \Big/ \left(\sum_i |\sigma_i|/\sqrt{\kappa_i}\right) = \left(\tau + \sum_i \frac{\sigma_i}{\kappa_i}\right) \Big/ \left(\sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}}\right) . \tag{34}$$

Note that C depends symmetrically on the parameters of all the branches. The entropy change is

$$\Delta S = C^{-1} \sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}} , \tag{35}$$

so we obtain:

Theorem 3. The optimal rate of entropy production along branch i is the constant

$$dS_i/dt = [C(C - \mathrm{sgn}\sigma_i/\sqrt{\kappa_i})]^{-1} . \tag{36}$$

As mentioned in Sec. IV, this constant depends on the best conductance κ_i.

In the slow-process limit $\tau_i \gg |\sigma_i|/\kappa_i$ (cf. Sec. VII A), $\Delta S = \sum_i \sigma_i^2/\kappa_i \tau_i$, so we obtain the primed equations above without the substitution defined in Eq. (28). Thus in this limit

$$\tau_i = C|\sigma_i|/\sqrt{\kappa_i} , \tag{33'}$$

and we get

Corollary 3.

$$dS_i/dt = C^{-2} ; \tag{36'}$$

i.e., the optimal rate of entropy production is in the slow-process limit the same for all branches of the cycle.

By comparing Eqs. (33), (36), with (33'), (36'), one sees that if the processes are driven faster than the "natural thermal transfer times," $|\sigma_i|/\kappa_i$, the optimal rate of entropy production will vary from branch to branch, unless heat is transferred in the same direction ($\mathrm{sgn}\sigma_i = \mathrm{sgn}\sigma_j$) through the same heat conductances ($\kappa_i = \kappa_j$). Equation (33) implies that the system spends most time on branches with large entropy flows or small heat conductances.

The expression for ΔS assumes a nice form for long times $\tau \gg |\sum_i (\sigma_i/\kappa_i)|$. Then we get from Eqs. (33)–(35), the following:

Theorem 4.

$$\Delta S = \left(\sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}}\right)^2 /\tau \geq \left(\sum_i |\sigma_i|\right)^2 /\kappa\tau , \tag{37}$$

where $\kappa = \max(\kappa_1, \ldots, \kappa_N)$. Note that this quantity depends only on the variation in the entropy of the working fluid $\sum_i |\sigma_i|$, or in other words, the total amount of entropy transferred in the cycle.

Tolman and Fine[13] have proven that the upper bound on the work produced by a process which generates entropy ΔS at discharge temperature T_0 is

$$W \leq W_{\mathrm{rev}} - T_0 \Delta S , \tag{38}$$

where W_{rev} is the theoretical work output for the corresponding lossless process.[16] Combining this with Eq. (37) we find the upper bound for our process.

Corollary 4.

$$W \leq W_{\mathrm{rev}} - T_0 \left(\sum_i |\sigma_i|\right)^2 /\kappa\tau . \tag{39}$$

VIII. REAL ENGINE CONSTRAINTS

The results obtained in Sec. VII and summarized in Sec. V are based on a picture of a heat engine as a system operating in a cycle which is made of distinct branches. Each branch is characterized by the change in the entropy of the system. Real engines are of course subjected to different constraints, e.g., the volume of the cylinder, the permissible working temperature and pressure ranges, etc. Such constraints can usually be specified in terms of the state of the working fluid in the extreme corners of the cycle. For example, a Carnot cycle can be characterized by the high and low temperatures and volumes, which define the state of the working gas at the starting point of each isotherm. We shall refer to such constraints as *corner constraints*.

Consider now a cycle which is supposedly optimized under some given real engine constraints. Focusing on a particular branch, we consider altering the path on this branch alone, while keeping the rest of the cycle fixed. In particular, this implies that the initial and final states of the working fluid on the special branch are constrained, as is the time to be spent on this branch. Suppose that by such a change the total entropy produced along this branch is lowered. This would obviously imply that the total entropy produced during the cycle operation is lowered and thus contradict our assumption that we started with the optimal cycle. *Thus each branch of a cycle optimized (with respect to total entropy production) under any corner constraints has to satisfy Theorem 1 (Sec. V): The optimal path is that on which entropy is produced at a constant rate.*

Next, consider the cycle as a whole. In the study of heat engines, enough information is usually provided to enable us to construct the corresponding reversible cycle (which has traditionally served as a basis for comparison with the actual work produced). The indicator diagram (the path of the working fluid in state space) of this reversible cycle also defines the state of the environment, which is in equilibrium with the working fluid at each point. Restrictions which define the indicator diagram may be specified either in terms of the working fluid or in terms of the environment.

For finite time cycles, we should distinguish between constraints imposed on the working fluid and constraints imposed on the environment. If the set of constraints used to define a reversible cycle is imposed on the working fluid alone, the indicator diagram of the latter (and therefore the set $\{\sigma_i\}$) is completely specified. In such cases the procedure described in Sec. VII is sufficient and the results provide the necessary conditions for minimum total entropy production. These conditions give the time-dependent behavior of the working fluid and of the environment (temperature of a reservoir, load on a piston, etc.).

In the more general case where engine limitations are given in part or in full in terms of the environment (e.g., temperature of a reservoir) the problem becomes more difficult. Now the set $\{\sigma_i\}$ is no longer given. We can obtain the σ_i's in terms of the τ_i's from the given restrictions, the optimal operation conditions [Eq. (25)], and the equations of state of the working fluid.

Example: Consider a Carnot-type cycle composed of two isothermal branches (characterized by temperatures T_1^{ex} and T_3^{ex} of the external reservoirs) and two adiabatic branches. We assume that the working fluid is an ideal gas with constant heat capacity C_v. Equation (25) implies for the isothermal branches

$$T_1 = T_1^{ex}/(1+\sigma_1/\kappa_1\tau_1), \tag{40}$$

$$T_3 = T_3^{ex}/(1+\sigma_3/\kappa_3\tau_3). \tag{41}$$

On the adiabatic branches $\sigma_2=\sigma_4=\tau_2=\tau_4=0$. The closure condition for the cycle $\sum_i \sigma_i = 0$ implies

$$\sigma_1 = -\sigma_3 \equiv \sigma. \tag{42}$$

Finally, the ideal-gas equations of state lead to

$$\sigma = R\ln(V^{max}/V^{min}) + C_v \ln(T_3/T_1), \tag{43}$$

where V^{max} and V^{min} are the largest and smallest volumes of the cylinder. From Eqs. (40), (41), and (43), we get

$$\sigma = \sigma_{rev} + C_v \ln\left(\frac{1+\sigma/\kappa_1\tau_1}{1-\sigma/\kappa_3\tau_3}\right), \tag{44}$$

where

$$\sigma_{rev} = R\ln(V^{max}/V^{min}) + C_v \ln(T_3^{ex}/T_1^{ex}). \tag{45}$$

If the compression ratio V^{max}/V^{min} is given as an additional constraint, Eq. (44) provides an expression for σ as a function of τ_1 and τ_3. Alternatively, if the maximum pressure P^{max} and the maximum volume are given as constraints rather than the compression ratio, Eq. (44) is replaced by (using $P^{max}V^{min} = nRT_1$)

$$\sigma = \sigma'_{rev} + C_P \ln(1+\sigma/\kappa_1\tau_1) - C_v \ln(1-\sigma/\kappa_3\tau_3), \tag{46}$$

where

$$\sigma'_{rev} = R\ln\left(\frac{V^{max}P^{min}}{nR}\right) + C_v \ln T_3^{ex} - C_P \ln T_1^{ex} \tag{47}$$

is a constant.

In general the σ_i's are complicated functions of the τ_i's. To minimize the total entropy production

$$\Delta S = \sum_{i=1}^{N} \frac{\sigma_i^2/\kappa_i\tau_i}{1+\sigma_i/\kappa_i\tau_i}, \tag{48}$$

subject to $\sum_i \tau_i = \tau$, we must use

$$\frac{\partial\Delta S}{\partial\tau_i} + \sum_j \frac{\partial\Delta S}{\partial\sigma_j}\frac{\partial\sigma_j}{\partial\tau_i} = \lambda, \tag{49}$$

for the Lagrange multiplier λ, rather than

$$\partial\Delta S/\partial\tau_i^1 = \lambda \tag{50}$$

as was done in Sec. VII C.

For infinitely slow operation, the σ_i's are given as properties of the corresponding reversible cycle. Assuming that $\{\sigma_i(\tau_1 \ldots \tau_N)\}$ $(i=1,\ldots,N)$ are continuously differentiable functions of the variables $\{1/\tau_i\}$, we can write

$$\sigma_i = \sigma_i^{rev} + \sum_{j=1}^{N} b_{ij}\frac{1}{\tau_j} + \cdots. \tag{51}$$

This leads to

$$\partial\sigma_i/\partial\tau_j = -b_{ij}/\tau_j^2 + \cdots. \tag{52}$$

Also, in the slow-process limit Eq. (26) in the form $\Delta S = \sum_j \sigma_j^2/\kappa_j\tau_j + \cdots$ implies

$$\left(\frac{\partial\Delta S}{\partial\tau_j}\right)_{\{\sigma_i\}} = -\frac{\sigma_j^2}{\kappa_j\tau_j^2} + \cdots \tag{53}$$

and

$$\left(\frac{\partial\Delta S}{\partial\sigma_j}\right)_{\{\tau_i\}} = \frac{2\sigma_j}{\kappa_j\tau_j} + \cdots. \tag{54}$$

The terms omitted in Eqs. (51)–(54) are of higher order in the $(1/\tau_j)$'s. To the lowest order in these variables we have

$$\sum_j \frac{\partial\Delta S}{\partial\sigma_j}\frac{\partial\sigma_j}{\partial\tau_j} = -\sum_j 2b_{ji}\frac{\sigma_j}{\kappa_j}\frac{1}{\tau_j\tau_i^2}, \tag{55}$$

which for large τ_i's may be disregarded relative

to the right-hand side of Eq. (53). This is possible provided

$$\tau_j \gg \frac{2b_{ij}\sigma_j}{\sigma_i^2}\,\frac{\kappa_i}{\kappa_j} \sim \frac{b_{ij}}{\sigma_j}\,. \tag{56}$$

For the Carnot cycle where $\sigma_1 = -\sigma_3 = \sigma_{\rm rev}$, we obtain from Eqs. (44) and (51),

$$b_j = \sigma_{\rm rev} C_v/\kappa_j\,, \tag{57}$$

so that the long-time condition (56) takes the form

$$\tau_j \gg C_v/\kappa_j\,. \tag{58}$$

Subject to this condition, we may keep the σ_i's constant while taking derivatives of ΔS with respect to the τ_i's and to the same approximation, the optimization procedure of Sec. VII C is valid.

To end this section, we stress again that there exist reasonable constraints (e.g., for the Otto or the Diesel cycle) which imply constant σ_i and thus justify the analysis of Sec. VII C even for short times.

IX. DERIVATION FOR GENERAL FLOWS

A. One branch

Consider the exchange of the generalized fluxes $\vec{\mathrm{j}} = (j_1, j_2, \ldots, j_k, \ldots,)$ driven by the forces $\vec{\mathrm{X}} = (X_1, X_2, \ldots, X_k, \ldots)$ between the appropriate reservoirs and the system. By our assumptions, there is no internal entropy production, so all irreversibility resides at the boundary. We assume that the fluxes have a phenomenological relationship $j_k(\vec{\mathrm{X}})$ to the forces. These relationships are not necessarily linear as in traditional irreversible thermodynamics close to equilibrium. We take the forces at the boundary as control variables and assume that the fluxes are functions only of the forces X_k, not of time or of any time derivatives of the forces. Thus we want to minimize the entropy produced.

$$\Delta S = \int_0^\tau \sum_k j_k X_k\, dt = \int_0^\tau \vec{\mathrm{j}}\cdot\vec{\mathrm{X}}\, dt\,, \tag{59}$$

for given integrated flows,

$$J_k = \int_0^\tau j_k dt\,. \tag{60}$$

This gives the Lagrangian

$$L = \sum_k j_k(\vec{\mathrm{X}}) X_k - \sum_k \lambda_k j_k(\vec{\mathrm{X}}) \tag{61}$$

and Euler equations

$$\frac{\partial L}{\partial X_l} = j_l(\vec{\mathrm{X}}) + \sum_k (X_k - \lambda_k)\,\frac{\partial j_k(\vec{\mathrm{X}})}{\partial X_l} = 0\,. \tag{62}$$

The phenomenological relationships $j_k(\vec{\mathrm{X}})$ can now be used to calculate $\partial j_k(\vec{\mathrm{X}})/\partial X_l$ and solve Eq. (62) for the forces X_l. Again the Euler equations are (coupled) algebraic equations so that the solutions, however complicated they may be, will be independent of time. This implies that also $dS/dt = \vec{\mathrm{j}}(X)\cdot\vec{\mathrm{X}}$ is a constant. Thus we deduce in general the following:

Theorem 1′: Minimum total entropy production for a process with given net fluxes implies constant entropy production rate along any one branch.

This is the general version of Theorem 1. If the j_k are independent and linear in $\vec{\mathrm{X}}$, the solution of Eq. (62) comes from solving the determinental (secular) equation for the X_l, whereas if the j_k are independent but nonlinear, the solution of Eq. (62) is the point set of intersections of the surfaces defined by (62).

B. Consecutive branches

We have from Eq. (60) for consecutive branches

$$\Delta S = \sum_i \Delta S_i = \sum_i (\vec{\mathrm{j}}_i\cdot\vec{\mathrm{X}}_i)\tau_i = \sum_i \vec{\mathrm{J}}_i\cdot\vec{\mathrm{X}}_i\,, \tag{63}$$

since the fluxes and forces along each branch are constant. Unless we know the functional form of $\vec{\mathrm{X}}_i(\vec{\mathrm{J}}_i/\tau_i)$, we cannot optimize Eq. (63) with respect to the τ_i, so let us at this point assume the relationship to be linear

$$\vec{\mathrm{j}} = \underline{L}\vec{\mathrm{X}}\,,\quad \vec{\mathrm{X}} = \underline{L}^{-1}\vec{\mathrm{j}}\,, \tag{64}$$

where $\underline{L}$ is the usual matrix of phenomenological coefficients. Then

$$\Delta S = \sum_i \vec{\mathrm{J}}_i \underline{L}^{-1} \vec{\mathrm{J}}_i/\tau_i \equiv \sum_i \alpha_i/\tau_i\,, \tag{65}$$

where the $\{\alpha_i\}$ do not depend on time. Optimization of Eq. (65) subject to Eq. (27), $\tau = \sum_i \tau_i$ yields

$$\tau_i = \left(\tau \Big/ \sum_l \sqrt{\alpha_l}\right)\sqrt{\alpha_i}\,, \tag{66}$$

so that

$$\Delta S = \left(\sum_i \sqrt{\alpha_i}\right)^2/\tau \tag{67}$$

and

$$dS_i/dt = \left(\sum_i \sqrt{\alpha_i}\right)^2/\tau^2\,, \tag{68}$$

which is the same constant for all branches (Corollary 1′). The linearity of Eq. (64) and the constancy of $\underline{L}$ correspond to the slow process limit in Sec. VII A.

X. DISCUSSION

In the sections above, we have repeatedly minimized the total entropy production in a heat-engine process subject to only thermal resistance losses.

We found that optimal operation implies constant entropy production rate on each branch. For slow operation, the requirement of minimum total entropy production implies that the entropy production rate is constant for the entire cycle.

The results further show that for optimal operation we should subject the working fluid to a constant thermal force on each branch. The required constant thermal force depends however on our choice of heat transfer law. If Newton's law of heat conduction holds, we need to hold T^{ex}/T constant. If we accept the heat-conduction law of irreversible thermodynamics, we need $(1/T)-(1/T_{ex})=$ constant. Newton's law is probably more reliable here.

Our solution for the one branch behavior of the optimal cycle is very general since we do not require any equations of state for the working fluid. The same is true for the long-time solution for the cycle as a whole. The general solution however, does depend on the detailed properties of the working fluid as was demonstrated in Sec. VIII. Note that in any case the results are not necessarily restricted to a gas in a cylinder and should apply for any engine.

The limitations imposed on the efficiency of operation by finite thermal conductance are significant. For realistic values of the parameters,[19] $\sigma=10$ J/K and $\kappa=200$ J/K sec in a Carnot-type engine working between 700 and 300 K with a cycle time of $\tau=1$ sec, we find (see Appendix B) that the efficiency is reduced to 47% from the reversible value of 57%. The efficiencies of the best actual heat engine processes with similar σ and κ are 40%[4] and thus compare favorably with the optimal engine with finite heat conductance.

The results described in the present paper differ in two important respects from previous work aimed at establishing limits on the quality of operation of finite time heat engines. The first difference is that our results apply to arbitrary heat engines, whereas most of the previous work[1,3-7] dealt only with Carnot-type cycles, i.e., cycles working between two constant temperature reservoirs. The second difference is our choice of objective function. Previous works have maximized efficiency and power in finite time heat engines. We minimized the entropy production and showed that this is equivalent to minimizing the loss of availability. Both the relationship to properties of many steady-state systems[20] and the connection to practical minimization of loss of availability [9c-9e] motivate this choice or criterion. It is, however, not equivalent to maximizing efficiency or power. For example, unlike the efficiency, the total entropy production criterion does not count heat at all temperatures equally. Efficiency and power by their nature define short-term goals. Total entropy production or availability corresponds to a longer range goal of preserving natural resources. Each of these criteria of merit has legitimacy and defines operational goals for the engine. A quantitative comparison between these and other criteria of merit will be provided in another publication, where we also discuss the problem of choosing among these criteria under a given price schedule.[9f]

The assumptions used in our formalism are standard. With few exceptions, mentioned below, the assumptions under which most optimal finite time operation problems have been attacked are, no friction, no internal dissipation, and neglect of inertial effects. An approach to optimal engine operation which takes friction into account has been described by three of us using the tricycle space formalism.[3] A model which includes internal irreversibility in a simplified manner has been treated by Richter and Ross.[21] The first of these works does not yield an explicit solution for the time operation of the engine, while the second is based on a highly simplified model. Inertial effects have been taken into account in Refs. 6 and 7.

In our model the working fluid is characterized by the single parameter σ, its entropy capacity. This is the simplest possible viewpoint short of using no parameters, as was done by Curzon and Ahlborn[4] and in the tricycle formalism.[3]

Our result states that the "best process" is associated with a constant rate of entropy production. This is reminiscent of Prigogine's theorem of irreversible thermodynamics which states[22] that the entropy production rate is minimum at near-equilibrium steady states. Both results are associated with variational principles. However the approach of Prigogine ("irreversible thermodynamics") involves instantaneous quantities while our formalism ("finite-time thermodynamics") investigates the extrema of integrals over time. It is interesting to note that both theorems are obtained under fairly similar assumptions. (In fact our results are in some sense more general; as we saw, the single branch results hold even when the phenomenological equations between flows and forces are nonlinear, so long as there is no internal dissipation.)

In the present work we limited ourselves to simple nonequilibrium situations. In particular, we disregarded irreversible processes associated with spatial inhomogeneities of the system. It will be interesting to investigate the generalization of the principle of constant entropy production rate to such cases which are encountered in processes involving internal dissipation.

Finally, we note that reversible bounds on work production have provided us with such fertile concepts as entropy and thermodynamic temperature.

The possibility of using finite time bounds as sources of new physical concepts should not be dismissed. We believe that the present article makes a start in this direction.

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APPENDIX A: THE PROPORTIONALITY BETWEEN LOSS OF AVAILABILITY AND ENTROPY PRODUCTION

Here we prove that the loss of availability associated with an irreversible thermal interaction is proportional to the entropy production. Thus minimizing the loss of availability is equivalent to minimizing the entropy production.

First consider N systems, each with constant heat capacity C and at different temperatures T_i. When they interact to come to equilibrium at the common temperature T_f, their respective change of entropy is

$$\Delta S_i = \int_{T_i}^{T_f} C/T\, dT = C \ln(T_f/T_i) . \tag{A1}$$

For a reversible interaction the total change in entropy vanishes:

$$\sum_i \Delta S_i = \sum_i C \ln(T_f/T_i) = C\left(N \ln T_f - \sum_i \ln T_i\right) = 0 , \tag{A2}$$

which defines the final temperature

$$T_f = \left(\prod_i T_i\right)^{1/N} . \tag{A3}$$

The availability A of the collection of systems is the maximum work which can be obtained from their interaction. Conservation of energy yields

$$A = W_{\max} = -\sum_i Q_i = \sum_i C(T_i - T_f) = CN\left[\sum_i T_i/N - \left(\prod_i T_i\right)^{1/N}\right] . \tag{A4}$$

As an irreversible interaction between the systems, let two of them come to equilibrium without work production. Their common final temperature will be

$$T_1' = T_2' = \tfrac{1}{2}(T_1 + T_2) \tag{A5}$$

and the availability of the total system is

$$A' = CN\left[\sum_i T_i/N - \left(\tfrac{1}{4}(T_1+T_2)^2 \prod_{i=3}^{N} T_i\right)^{1/N}\right] . \tag{A6}$$

The loss of availability is thus

$$\Delta A = A - A' = CN\left(\prod_{i=1}^{N} T_i\right)^{1/N}\left[\left(\frac{(T_1+T_2)^2}{4T_1T_2}\right)^{1/N} - 1\right] . \tag{A7}$$

The entropy produced in the irreversible interaction is

$$\Delta S = \int_{T_1}^{T_1'} C/T\, dT + \int_{T_2}^{T_2'} C/T\, dT = C \ln \frac{(T_1+T_2)^2}{4T_1T_2} , \tag{A8}$$

so that

$$\frac{\Delta A}{\Delta S} = N\left(\prod_i T_i\right)^{1/N}\left[\left(\frac{(T_1+T_2)^2}{4T_1T_2}\right)^{1/N} - 1\right] \Big/ \ln \frac{(T_1+T_2)^2}{4T_1T_2} . \tag{A9}$$

This depends not only on all the system temperatures but also on the nature of the irreversible process. However, in the limit of many systems we may use

$$\lim_{N\to\infty}\left(\frac{N(X^{1/N}-1)}{\ln X}\right) = 1 \tag{A10}$$

to obtain

$$\frac{\Delta A}{\Delta S} \to \left(\prod_i T_i\right)^{1/N} . \tag{A11}$$

Thus the geometric mean of the temperatures of systems provides the proportionality constant between the entropy production and the loss of availability. If all but a small number of systems have the same temperature T_0, they constitute a reference reservoir, and then

$$\Delta A/\Delta S = T_0 . \tag{A12}$$

We can prove Eq. (A12) also for the more general case of temperature-dependent heat capacities $C_i = C_i(T)$. As before, the common temperature T_f after a reversible interaction is obtained from

$$\sum_i \Delta S_i = \sum_i \int_{T_i}^{T_f} C_i(T)/T\, dT = 0 , \tag{A13}$$

although we cannot give an explicit expression for T_f. As in Eq. (A4) the availability is

$$A = W_{\max} = -\sum_i Q_i = \sum_i \int_{T_i}^{T_f} C_i(T)\,dT\,. \tag{A14}$$

We now let systems 1 and 2 interact irreversibly to arrive at temperatures T_1' and T_2'. A subsequent reversible interaction between all system will lead to a different final temperature T_f' such that

$$\sum_i \Delta S_i' = \sum_i \int_{T_i'}^{T_f'} C_i(T)/T\,dT = 0\,. \tag{A15}$$

Taking the difference between Eqs. (A13) and (A15), we see that

$$\left(\int_{T_1}^{T_1'} + \int_{T_2}^{T_2'} + \sum_i \int_{T_f'}^{T_f}\right) C_i(T)/T\,dT = 0\,. \tag{A16}$$

Similarly, the loss of availability is

$$\Delta A = A - A' = -\left(\int_{T_1}^{T_1'} + \int_{T_2}^{T_2'} + \sum_i \int_{T_f'}^{T_f}\right) C_i(T)\,dT$$

$$= -\sum_i \int_{T_f'}^{T_f} C_i(T)\,dT\,. \tag{A17}$$

The entropy produced is

$$\Delta S = \left(\int_{T_1}^{T_1'} + \int_{T_2}^{T_2'}\right) C_i(T)/T\,dT$$

$$= -\sum_i \int_{T_f'}^{T_f} C_i(T)/T\,dT\,, \tag{A18}$$

so that

$$\frac{\Delta A}{\Delta S} = \left(\sum_i \int_{T_f'}^{T_f} C_i(T)\,dT\right) \Big/ \left(\sum_i \int_{T_f'}^{T_f} C_i(T)/T\,dT\right). \tag{A19}$$

Consider the case where all systems $i \geq 3$ are combined into a single reservoir of temperature T_0 and heat capacity C_0. In the limit $C_1,\ C_2 \ll C_0$, we have $T_f \approx T_f' \approx T_0$, and

$$\Delta A/\Delta S = [C_0(T_0)(T_f - T_f')]/[(T_f - T_f')C_0(T_0)/T_0] = T_0\,, \tag{A20}$$

which again proves that the entropy production and the loss of availability are proportional to each other.

APPENDIX B: NUMERICAL RESULTS FOR THE FINITE-TIME CARNOT CYCLE

An important advantage of the formalism presented in this paper is that it allows one to calculate all quantities related to the finite-time operation of a model heat engine. Furthermore, the required calculations are well within the capacity of todays programmable calculators. Below we illustrate this feature of our formalism with the numerical results for an ideal-gas working fluid undergoing a Carnot cycle working between given temperatures T_1^{ex} and T_3^{ex}, with a given compres-

TABLE II. Numerical results for the finite-time Carnot cycle with minimum entropy production.

Given engine data	τ (sec)	η	τ_1/τ	Exact results T_1 (K)	T_3 (K)	σ (J/K)	W (J)	W_{rev} (J)	$4T_0\sigma^2/\kappa\tau$ (J)	τ_1/τ	Constant σ results T_1 (K)	T_3 (K)	σ (J/K)
$T_1^{ex}=700$ K, $T_3^{ex}=300$ K	0.5	0.1794	0.3926	496.9	407.7	16.78	1497	4766	3232	0.3356	469.6	398.8	17.22
$V^{max}/V^{min}=10$, $\kappa=209$ J/sec K	1	0.4671	0.4556	625.4	333.3	11.37	3321	4062	741.0	0.4456	623.9	332.6	11.37
$\sigma_{rev}=8.633$ J/K, $\eta_{rev}=0.5714$	2	0.5293	0.4791	667.3	314.1	9.811	3465	3741	276.0	0.4766	667.2	314.1	9.811
$\tau_{min}=0.47$ sec	4	0.5522	0.4896	684.7	306.6	9.184	3472	3593	121.0	0.4890	684.6	306.6	9.184
$T_1^{ex}=400$ K, $T_3^{ex}=300$ K	1.35	0.0166	0.4426	347.1	341.3	19.06	109.7	1654	1543	0.4325	346.0	340.5	19.07
$V^{max}/V^{min}=10$, $\kappa=209$ J/sec K	2	0.1106	0.4616	366.3	325.7	17.80	721.2	1630	908.4	0.4575	366.0	325.5	17.80
$\sigma_{rev}=15.66$ J/K, $\eta_{rev}=0.25$	4	0.1878	0.4812	384.1	312.0	16.66	1202	1600	397.9	0.4801	384.1	311.9	16.66
$\tau_{min}=1.3$ sec	8	0.2205	0.4906	392.3	305.8	16.14	1396	1583	186.6	0.4904	392.3	305.8	16.14
$T_1^{ex}=400$ K, $T_3^{ex}=300$ K	0.4	0.0246	0.4591	350.0	341.4	5.487	47.28	480.1	431.8	0.4340	347.2	339.6	5.522
$V^{max}/V^{min}=2$, $\kappa=209$ J/sec K	1	0.2075	0.4886	389.0	308.3	2.881	232.6	280.2	47.70	0.4862	389.0	308.3	2.881
$\sigma_{rev}=2.189$ J/K, $\eta_{rev}=0.25$	2	0.2319	0.4941	395.2	303.6	2.488	228.1	245.8	17.57	0.4941	395.2	303.6	2.488
$\tau_{min}=0.39$ sec	4	0.2416	0.4974	397.8	301.7	2.329	223.8	231.6	7.782	0.4972	397.8	301.7	2.329

sion ratio $V^{\max}/V^{\min}$, heat conductance $\kappa \equiv \kappa_1 = \kappa_2$, and cycle time τ. The results for a few representative values of the parameters are shown in Table II. Note that the results of the exact calculations and the constant σ calculations are very close even for very short times, e.g., the minimum cycle time $\tau_{\min}$ for the engine. (As the cycle time τ is decreased, the engine produces less work. $\tau_{\min}$ is defined as the cycle time for which zero work is produced.) Note further that the equation

$$W = W_{\text{rev}} - 4T_0\sigma^2/\kappa\tau \tag{B1}$$

is valid to three significant figures for all our data. This means that the bound

$$W \leq W_{\text{rev}} - 4T_0\sigma^2/\kappa\tau \tag{B2}$$

given for large times by Corollary 2 [Eq. (7)], may be assumed valid quite generally.

We now describe how the data in these tables were calculated. As shown in the example of Sec. VIII, the entropy capacity $\sigma = \sigma_1 = -\sigma_3$ of such an engine is related to the times τ_1 and τ_3 spent on the heat exchange branches of the cycle by Eqs. (44) and (45),

$$\sigma = \sigma_{\text{rev}} + C_v \ln\left(\frac{1+\sigma/\kappa\tau_1}{1-\sigma/\kappa\tau_3}\right), \tag{B3}$$

where

$$\sigma_{\text{rev}} = R\ln(V^{\max}/V^{\min}) + C_v \ln(T_3^{\text{ex}}/T_1^{\text{ex}}). \tag{B4}$$

Since we are given the total cycle time $\tau = \tau_1 + \tau_3$, our optimization problem is to find τ_1 such that the total entropy production [Eq. (26)]

$$\Delta S = \sum_i \frac{\sigma_i^2/\kappa_i\tau_i}{1+\sigma_i/\kappa_i\tau_i} = \frac{\sigma^2}{\kappa\tau_1+\sigma} + \frac{\sigma^2}{\kappa\tau_3-\sigma} \tag{B5}$$

is minimized.

The numerical optimization proceeds as follows. Choosing a specific value of τ_1, Eq. (B3) can be solved iteratively for σ by substituting a guess value σ_{guess} on the right-hand side of (B3), and using the resulting σ equal to the left-hand side of (B3) as the next guess. This iterative scheme converges quickly, and we can use the obtained value of σ to evaluate ΔS by Eq. (B5). This procedure is repeated for different choices of τ_1, until τ_1^{opt} is determined to the desired accuracy. Once τ_1^{opt} is known, we can evaluate σ and ΔS from Eqs. (B3)–(B5), and the other engine parameters from

$$T_1 = T_1^{\text{ex}}/(1+\sigma/\kappa\tau_1), \tag{B6}$$

$$T_3 = T_3^{\text{ex}}/(1-\sigma/\kappa\tau_3), \tag{B7}$$

$$\eta_{\text{rev}} = 1 - T_3^{\text{ex}}/T_1^{\text{ex}}, \tag{B8}$$

$$\eta = 1 - T_3/T_1, \tag{B9}$$

$$W = \sigma(T_1 - T_3), \tag{B10}$$

$$W_{\text{rev}} = \sigma T_1 \eta_{\text{rev}}, \tag{B11}$$

where η denotes efficiency and W denotes work. The results of such calculations appear in Table II under the heading "exact results." Alternatively, we can use the computational scheme by assuming that σ is a constant (Sec. VIIC). Subject to this approximation, we can eliminate the search for τ_1^{opt} and use Eqs. (33) and (34) to find

$$\tau_i^{\text{opt}} = C\frac{|\sigma_i|}{\sqrt{\kappa_i}} - \frac{\sigma_i}{\kappa_i}, \tag{B12}$$

with

$$C = \left(\tau + \sum_i \frac{\sigma_i}{\kappa_i}\right)\Big/\left(\sum \frac{|\sigma_i|}{\sqrt{\kappa_i}}\right). \tag{B13}$$

For our example, (B12) and (B13) reduce to

$$\tau_1^{\text{opt}} = \tfrac{1}{2}\tau - \sigma/\kappa, \tag{B14}$$

$$\tau_2^{\text{opt}} = \tfrac{1}{2}\tau + \sigma/\kappa. \tag{B15}$$

The iterative scheme for the constant σ calculations is based on Eqs. (B3), (B14), and (B15). A guess value of σ is used in Eqs. (B14) and (B15) to get τ_1 and τ_3 which give a better σ from Eq. (B3). This scheme is much faster as it eliminates the need to search for τ_1^{opt}. The results are presented in this table under the heading "constant-σ results."

Since the results of both types of calculations depend only on the product $\kappa\tau$ rather than on the values of κ or τ separately, one can easily obtain results for κ' from the data in the table by altering the corresponding τ to $\tau' = \kappa\tau/\kappa'$.

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[14]Fixed mechanical coupling is defined by a constraint that some mechanical parameter of the working fluid remains constant. For a gaseous working fluid, the interesting special cases are isobaric (P = const), isometric (V = const), or polytropic (PV^n = const), but any $g(P,V)$ = const also satisfies our definition of fixed mechanical coupling. For different working fluids, such as may be used in cooling by adiabatic demagnetization for example, relevant cases of fixed mechanical coupling might involve constant magnetic field or constant magnetization.

[15]In Eq. (5) and in the remainder of the paper, S refers to the entropy of the universe, i.e., of system plus surroundings.

[16]For example consider a heat engine working between a heat source at constant temperature T_H and a heat sink at constant temperature T_C. If in one cycle the amount of heat Q^H is taken from the hot source and the amount Q^C is added to the cold source, then W_{rev} is the sum of the works associated with the reversible engines in which the hot and cold sources exchange the same heats Q^H and Q^C, and with the environment (of temperature T_0) playing the role of the other reservoir. Thus

$$W_{rev} = Q^H(1 - T_0/T_H) - Q^C(1 - T_0/T_C).$$

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